

**IN THE UNITED STATES OF AMERICA
PATENT AND TRADEMARK OFFICE**

APPLICANT: Schucker, R.

EXAMINER: Singh, Prem

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TITLE: Desulfurization of Petroleum Streams Using Metallic Sodium

Declaration of Dr. Robert C. Schucker

County of Montgomery:

State of Texas

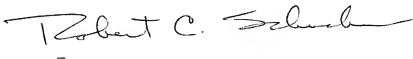
I, Robert C. Schucker, declare as follows:

1. I am a resident of the state of Texas and am of the age of majority;
2. I am an inventor of the invention in the above identified application;
3. I have a PhD in Chemical Engineering, and have worked as a practicing chemical engineer for over 30 years.
4. In the office action dated July 12, 2006 in the above application, the examiner has indicated that a solution of metallic sodium in liquid anhydrous ammonia is similar to sodium amide, hereafter referred to as sodamide (NaNH_2). This is incorrect. Sodamide is physically, structurally and chemically different from metallic sodium dissolved in ammonia, as will be shown.
5. First, the species are acknowledged to be different as evidenced by the assignment of different CAS Numbers by the Chemical Abstracts Service, which has been given the responsibility of cataloguing chemicals. Sodium has a CAS number of [7440-23-5], ammonia has a CAS number of [7664-41-7]; and sodamide has a CAS number of [7782-92-5]. If two materials have different CAS numbers, they are not the same, by definition.

6. Secondly, their physical properties are different. Sodium metal has a melting point of 97.7 °C and a boiling point of 883°C. Ammonia has melting point of -77.72 °C and a boiling point of -33.34 °C. Sodamide has a melting point of 210 °C and a boiling point of 400 °C (see Wikipedia entry, attached hereto). As used in the Baird process, sodamide is a solid when mixed with the hydrocarbon feed, whereas the present invention uses a liquid solution of sodium in ammonia.
7. Their chemical structures are also different. Sodamide is an ionic compound wherein sodium is in the +1 valence state, while metallic sodium dissolved in ammonia is simply a solution of sodium metal in the zero valence state dissolved in ammonia. **The CRC Handbook of Chemistry and Physics**, 73rd Ed. (1993) indicates that the solubility of sodamide in liquid ammonia is only 0.1 grams in 100 grams ammonia (0.1 wt%); whereas, **the Kirk-Othmer Encyclopedia of Chemical Technology** indicates that at -33.5 C, 0.251 kg of sodium can be dissolved in 1.00 kg of ammonia (a 20 wt% solution).
8. Finally, sodium dissolved in ammonia and sodamide are vastly different in chemical reactivity. Sodium metal dissolved in ammonia reacts by donation of one electron; which is known to occur rapidly at very low temperatures. Loss of this one electron produces Na^{+1} as a product. Sodium metal can react with ammonia in the presence of a catalyst (typically iron or nickel) to produce sodamide, but in the absence of such a catalyst, this reaction is extremely slow at low temperatures contemplated in the invention.. It is important to understand that the sodamide is the reaction product, not the reactant. Sodamide is a salt; and in reactions that take place in hydrocarbons, where it cannot easily dissociate into its component ions, it reacts through sharing of electrons, similar to most thermal free radical reactions. This can only occur at elevated temperatures, as exemplified by Baird. Because sodium in sodamide has a valence of +1, and, because it

has already lost the only electron it can lose, it is much less reactive than metallic sodium (valence state of 0).

9. Sodamide is not physically, structurally or chemically similar to metallic sodium in solution in liquid ammonia. There is no motivation to replace sodamide in the desulfurization method described in Baird with metallic sodium/ammonia solution due to the substantial structural, physical and chemical differences of these two substances.
10. I hereby declare that all statements are made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.



Dr. Robert C. Schucker

September 21, 2006

Date

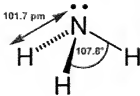


Ammonia

From Wikipedia, the free encyclopedia

Ammonia is a compound of nitrogen and hydrogen with the formula NH_3 . At standard temperature and pressure, ammonia is a gas. It is toxic and corrosive to some materials, and has a characteristic pungent odor. Ammonia used commercially is called *anhydrous ammonia* to distinguish it from ammonium hydroxide solution, which is *household ammonia*.

An ammonia molecule has a trigonal pyramid shape, as predicted by VSEPR theory. This shape gives the molecule an overall dipole moment, and makes it polar so that ammonia readily dissolves in water. The nitrogen atom in the molecule has a lone electron pair, and ammonia acts as a base. That means that, when in aqueous solution, it can take a proton from water to produce a hydroxide anion and an ammonium cation (NH_4^+), which has the shape of a regular tetrahedron. The degree to which ammonia forms the ammonium ion depends on the pH of the solution—at "physiological" pH (~7), about 99% of the ammonia molecules are protonated.

The main uses of ammonia are in the production of fertilizers, explosives and polymers. It is also an ingredient in certain household glass cleaners. Ammonia is found in small quantities in the atmosphere,

Ammonia	
 	
General	
Systematic name	Ammonia Azane (<i>See Text</i>)
Other names	Hydrogen nitride Spirit of hartshorn Nitrosil Vaporole
Molecular formula	NH_3
Molar mass	17.0304 g/mol
Appearance	Colourless gas with strong pungent odor
CAS number	[7664-41-7] [2] (http://webbook.nist.gov/cgi/cbook.cgi?ID=7664-41-7&Units=SI)
Properties	
Density and phase	0.6813 g/L, gas.
Solubility in water	89.9 g/100 ml at 0 °C.
Melting point	-77.73 °C (195.42 K)
Boiling point	-33.34 °C (239.81 K)
Acidity ($\text{p}K_a$)	≈34
Basicity ($\text{p}K_b$)	4.75
Structure	
Molecular shape	Terminus
Dipole moment	1.42 D
Bond angle	107.5°
Hazards	
MSDS	External MSDS
Main hazards	Toxic and corrosive.
NFPA 704	
Flash point	11 °C
R/S statement	R: R10, R23, R34, R50 S: S1/2, S16, S36/37/39, S45, S61
RTECS number	BO0875000
Supplementary data page	
Structure and properties	n , ϵ_p , etc.
Thermodynamic data	Phase behaviour Solid, liquid, gas

being produced from the putrefaction of nitrogenous animal and vegetable matter. Ammonia and ammonium salts are also found in small quantities in rainwater, while ammonium chloride (sal-ammoniac) and ammonium sulfate are found in volcanic districts; crystals of ammonium bicarbonate have been found in Patagonian guano. Ammonium salts also are found distributed through all fertile soil and in seawater. Substances containing ammonia, or that are similar to it, are called *ammoniacal*.

Spectral data	UV, IR, NMR, MS
Related compounds	
Other ions	Ammonium (NH_4^+)
	hydroxide (NH_4OH) chloride (NH_4Cl)
Related compounds	Hydrazine Hydrazoic acid Hydroxylamine Chloramine
	Except where noted otherwise, data are given for materials in their standard state (at 25 °C, 100 kPa) Infobox disclaimer and references

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History

Salts of ammonia have been known from very early times; thus the term *Hammoniacus* ^[1] appears in the writings of Pliny, although it is not known whether the term is identical with the more modern *sal-ammoniac*.^[1]

In the form of sal-ammoniac, ammonia was known to the alchemists as early as the 13th century, being mentioned by Albertus Magnus.^[2] It was also used by dyers in the Middle Ages in the form of fermented urine^[2] to alter the colour of vegetable dyes. In the 15th century, Basilius Valentinus showed that ammonia could be obtained by the action of alkalis on sal-ammoniac. At a later period, when sal-ammoniac was obtained by distilling the hoofs and horns of oxen and neutralizing the resulting carbonate with hydrochloric acid, the name "spirit of hartshorn" was applied to ammonia.^[2]

Gaseous ammonia was first isolated by Joseph Priestley in 1774 and was termed by him *alkaline air*; however it was acquired by the alchemist Basil Valentine.^[3] Eleven years later in 1785, Claude Louis Berthollet ascertained its composition.

The Haber process to produce ammonia from the nitrogen contained in the air was developed by Fritz Haber and Carl Bosch in 1909 and patented in 1910. It was first used on an industrial scale by the Germans during World War I,^[4] following the allied blockade that cut off the supply of nitrates from Chile. The ammonia was used to produce explosives to sustain their war effort.^[5]

Synthesis and production

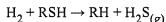
Because of its many uses, ammonia is one of the most highly-produced inorganic chemicals. There are dozens of chemical plants worldwide that produce ammonia. The worldwide ammonia production in 2004 was 109 million metric tonnes.^[6] the People's Republic of China produced 28.4% of the worldwide production followed by India with 8.6%, Russia with 8.4%, and the United States with 8.2%.^[6] About 80% or more of the ammonia produced is used for fertilizing agricultural crops.^[6]

Before the start of World War I most ammonia was obtained by the dry distillation^[7] of nitrogenous vegetable and animal waste products, including camel dung where it was distilled^[5] by the reduction of nitrous acid and nitrites with hydrogen; additionally, it was produced by the distillation of coal;^[5] and also by the decomposition of ammonium salts by alkaline hydroxides^[8] or by quicklime, the salt most generally used being the chloride (sal-ammoniac) thus:

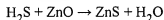


Today, the typical modern ammonia-producing plant first converts natural gas (i.e. methane) or liquified petroleum gas (such gases are propane and butane) or petroleum naphtha into gaseous hydrogen. Starting with a natural gas feedstock, the processes used in producing the hydrogen are:

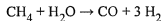
- The first step in the process is to remove sulfur compounds from the feedstock because sulfur deactivates the catalysts used in subsequent steps. Sulfur removal requires catalytic hydrogenation to convert sulfur compounds in the feedstocks to gaseous hydrogen sulfide:



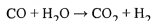
- The gaseous hydrogen sulfide is then absorbed and removed by passing it through beds of zinc oxide where it is converted to solid zinc sulfide:



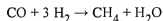
- Catalytic steam reforming of the sulfur-free feedstock is then used to form hydrogen plus carbon monoxide:

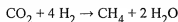


- The next step then uses catalytic shift conversion to convert the carbon monoxide to carbon dioxide and more hydrogen:

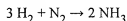


- The carbon dioxide is then removed either by absorption in aqueous ethanolamine solutions or by adsorption in pressure swing adsorbers (PSA) using proprietary solid adsorption media.
- The final step in producing the hydrogen is to use catalytic methanation to remove any small residual amounts of carbon monoxide or carbon dioxide from the hydrogen:





- To produce the desired end-product ammonia, the hydrogen is then catalytically reacted with nitrogen (derived from process air) to form anhydrous liquid ammonia. This step is known as the ammonia synthesis loop (also referred to as the Haber-Bosch process):



The steam reforming, shift conversion, carbon dioxide removal and methanation steps each operate at absolute pressures of about 25 to 35 bar, and the ammonia synthesis loop operates at absolute pressures ranging from 60 to 180 bar depending upon which proprietary design is used. There are many engineering and construction companies that offer proprietary designs for ammonia synthesis plants. Haldor Topsoe of Denmark, Lurgi AG of Germany, and Kellogg, Brown and Root of the United States are among the most experienced companies in that field.^[9]

Biosynthesis

In certain organisms, ammonia is produced from atmospheric N_2 by enzymes called nitrogenases. The overall process is called nitrogen fixation. Although it is unlikely that biomimetic methods will be developed that are competitive with the Haber process, intense effort has been directed toward understanding the mechanism of biological nitrogen fixation. The scientific interest in this problem is motivated by the unusual structure of the active site of the enzyme, which consists of an Fe_7MoS_9 ensemble.

Ammonia is also a metabolic product of amino acid deamination. In humans, it is quickly converted to urea, which is much less toxic. This urea is a major component of the dry weight of urine.

Properties

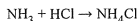
Ammonia is a colourless gas with a characteristic pungent smell; it is lighter than air, its density being 0.589 times that of air. It is easily liquefied; the liquid boils at -33.3°C , and solidifies at -77.7°C to a mass of white crystals. Liquid ammonia possesses strong ionizing powers ($\epsilon = 22$), and solutions of salts in liquid ammonia have been much studied. Liquid ammonia has a very high standard enthalpy change of vaporization (23.35 kJ/mol, *c.f.* water 40.65 kJ/mol, methane 8.19 kJ/mol, phosphine 14.6 kJ/mol) and can therefore be used in laboratories in non-insulated vessels at room temperature, even though it is well above its boiling point.

It is miscible with water. All the ammonia contained in an aqueous solution of the gas may be expelled by boiling. The aqueous solution of ammonia is basic. The maximum concentration of ammonia in water (a saturated solution) has a density of 0.880 g cm⁻³ and is often known as '.880 Ammonia'. Ammonia does not sustain combustion, and it does not burn readily unless mixed with oxygen, when it burns with a pale yellowish-green flame. At high temperature and in the presence of a suitable catalyst, ammonia is decomposed into its constituent elements. Chlorine catches fire when passed into ammonia, forming nitrogen and hydrochloric acid; unless the ammonia is present in excess, the highly explosive nitrogen trichloride (NCl_3) is also formed.

The ammonia molecule readily undergoes nitrogen inversion at room temperature - that is, the nitrogen atom passes through the plane of symmetry of the three hydrogen atoms; a useful analogy is an umbrella turning itself inside out in a strong wind. The energy barrier to this inversion is 24.7 kJ/mol in ammonia, and the resonance frequency is 23.79 GHz, corresponding to microwave radiation of a wavelength of 1.260 cm. The absorption at this frequency was the first microwave spectrum to be observed^[10].

Formation of salts

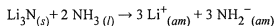
One of the most characteristic properties of ammonia is its power of combining directly with acids to form salts; thus with hydrochloric acid it forms ammonium chloride (sal-ammoniac); with nitric acid, ammonium nitrate, etc. However perfectly dry ammonia will not combine with perfectly dry hydrogen chloride, a gas, moisture being necessary to bring about the reaction.^[11]



The salts produced by the action of ammonia on acids are known as the ammonium salts and all contain the ammonium ion (NH_4^+).

Acidity

Although ammonia is well-known as a base, it can also act as an extremely weak acid. It is a protic substance, and is capable of dissociation into the **amide** (NH_2^-) ion, for example when solid lithium nitride is added to liquid ammonia, forming a lithium amide solution:



This is a Brønsted-Lowry acid-base reaction in which ammonia is acting as an acid.

Formation of other compounds

Ammonia can act as a nucleophile in substitution reactions. Amines can be formed by the reaction of ammonia with alkyl halides, although the resulting $-\text{NH}_2$ group is also nucleophilic and secondary and tertiary amines are often formed as by-products. Using an excess of ammonia helps minimise multiple substitution, and neutralises the hydrogen halide formed. Methylamine is prepared commercially by the reaction of ammonia with chloromethane, and the reaction of ammonia with 2-bromopropanoic acid has been used to prepare racemic alanine in 70% yield. Ethanolamine is prepared by a ring-opening reaction with ethylene oxide: the reaction is sometimes allowed to go further to produce diethanolamine and triethanolamine.

Amides can be prepared by the reaction of ammonia with a number of carboxylic acid derivatives. Acyl chlorides are the most reactive, but the ammonia must be present in at least a two-fold excess to neutralise the hydrogen chloride formed. Esters and anhydrides also react with ammonia to form amides. Ammonium salts of carboxylic acids can be dehydrated to amides so long as there are no thermally sensitive groups present: temperatures of 150–200 °C are required.

The hydrogen in ammonia is capable of replacement by metals, thus magnesium burns in the gas with the formation of magnesium nitride Mg_3N_2 , and when the gas is passed over heated sodium or potassium, sodamide, NaNH_2 , and potassamide, KNH_2 , are formed. Where necessary in substitutive nomenclature, IUPAC recommendations prefer the name **azane** to ammonia: hence chloramine would be named *chloroazane* in substitutive nomenclature, not *chloroammonia*.

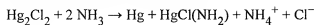
Ammonia as a ligand

Ammonia can act as a ligand in transition metal complexes. It is a pure σ -donor, in the middle of the spectrochemical series, and shows intermediate hard-soft behaviour. For historical reasons, ammonia is named **ammine** in the nomenclature of coordination compounds. Some notable ammine complexes include:

- **Tetraamminecopper(II)**, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, a characteristic dark blue complex formed by adding ammonia to solution of copper (II) salts.
- **Diamminesilver(I)**, $[\text{Ag}(\text{NH}_3)_2]^+$, the active species in Tollens' reagent. Formation of this complex can also help to distinguish between precipitates of the different silver halides: AgCl is soluble in dilute (2M) ammonia solution, AgBr is only soluble in concentrated ammonia solution while AgI is insoluble in aqueous solution of ammonia.

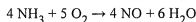
Ammine complexes of chromium(III) were known in the late 19th century, and formed the basis of Alfred Werner's theory of coordination compounds. Werner noted that only two isomers (*fac*- and *mer*-) of the complex $[\text{CrCl}_3(\text{NH}_3)_3]$ could be formed, and concluded that the ligands must be arranged around the metal ion at the vertices of an octahedron. This has since been confirmed by X-ray crystallography.

An ammine ligand bound to a metal ion is markedly more acidic than a free ammonia molecule, although deprotonation in aqueous solution is still rare. One example is the Calomel reaction, where the resulting amidomercury(II) compound is highly insoluble.



Uses

The most important single use of ammonia is in the production of nitric acid. A mixture of one part ammonia to nine parts air is passed over a platinum gauze catalyst at 850 °C, whereupon the ammonia is oxidized to nitric oxide.



The catalyst is essential, as the normal oxidation (or combustion) of ammonia gives dinitrogen and water: the production of nitric oxide is an example of kinetic control. As the gas mixture cools to 200–250 °C, the nitric oxide is in turn oxidized by the excess of oxygen present in the mixture, to give nitrogen dioxide. This is reacted with water to give nitric acid for use in the production of fertilizers and explosives.

In addition to serving as a fertilizer ingredient, ammonia can also be used directly as a fertilizer by forming a solution with irrigation water, without additional chemical processing. This later use allows the continuous growing of nitrogen dependent crops such as maize (corn) without crop rotation but this type of use leads to poor soil health.

Ammonia has thermodynamic properties that make it very well suited as a refrigerant, since it liquefies readily under pressure, and was used in virtually all refrigeration units prior to the advent of haloalkanes such as Freon. However, ammonia is a toxic irritant and its corrosiveness to any copper alloys increases the risk that an undesirable leak may develop and cause a noxious hazard. Its use in small refrigeration units has been largely replaced by haloalkanes, which are not toxic irritants and are practically not flammable. Ammonia continues to be used as a refrigerant in large industrial processes such as bulk icemaking and industrial food processing. Ammonia is also useful as a component in absorption-type refrigerators, which do not use compression and expansion cycles but can exploit heat differences. Since the implication of haloalkane being major contributors to ozone depletion, ammonia is again seeing increasing use as a refrigerant.

It is also sometimes added to drinking water along with chlorine to form chloramine, a disinfectant. Unlike chlorine on its own, chloramine does not combine with organic (carbon containing) materials to form carcinogenic halomethanes such as chloroform.

During the 1960s, Tobacco companies such as *Brown & Williamson* and *Philip Morris* began using ammonia in cigarettes. The addition of ammonia serves to enhance the delivery of nicotine into the blood stream. As a result the reinforcement effect of the nicotine was enhanced, increasing its addictive ability without actually increasing the portion of nicotine.^[12]

Ammonia's role in biologic systems and human disease

Ammonia is an important source of nitrogen for living systems. Although atmospheric nitrogen abounds, few living creatures are capable of utilizing this nitrogen. Nitrogen is required for the synthesis of amino acids, which are the building blocks of protein. Some plants rely on ammonia and other nitrogenous wastes incorporated into the soil by decaying matter. Others, such as nitrogen-fixing legumes, benefit from symbiotic relationships with rhizobia which create ammonia from atmospheric nitrogen.^[13]

Ammonia also plays a role in both normal and abnormal animal physiology. Ammonia is created through normal amino acid metabolism and is toxic in high concentrations. The liver converts ammonia to urea through a series of reactions known as the urea cycle. Liver dysfunction, such as that seen in cirrhosis, may lead to elevated amounts of ammonia in the blood (hyperammonemia). Likewise, defects in the enzymes responsible for the urea cycle, such as ornithine transcarbamylase, lead to hyperammonemia. Hyperammonemia contributes to the confusion and coma of hepatic encephalopathy as well as the neurologic disease common in people with urea cycle defects and organic acidurias.^[14]

Ammonia is important for normal animal acid/base balance. After formation of ammonium from glutamine, α -ketoglutarate may be degraded to produce two molecules of bicarbonate which are then available as buffers for dietary acids. Ammonium is excreted in the urine resulting in net acid loss. Ammonia may itself diffuse across the renal tubules, combine with a hydrogen ion, and thus allow for further acid excretion.^[15]

Liquid ammonia as a solvent

See also: Inorganic nonaqueous solvent

Liquid ammonia is the best-known and most widely studied non-aqueous ionizing solvent. Its most conspicuous property is its ability to dissolve alkali metals to form highly coloured, electrically conducting solutions containing solvated electrons. Apart from these remarkable solutions, much of the chemistry in liquid ammonia can be classified by analogy with related reactions in aqueous solutions. Comparison of the physical properties of NH_3 with those of water shows that NH_3 has the lower melting point, boiling point, density, viscosity, dielectric constant and electrical conductivity; this is due at least in part to the weaker H bonding in NH_3 and the fact that such bonding cannot form cross-linked networks since each NH_3 molecule has only 1 lone-pair of electrons compared with 2 for each H_2O molecule. The ionic self-dissociation constant of liquid NH_3 at $-50\text{ }^\circ\text{C}$ is approx. $10^{-33}\text{ mol}^2\cdot\text{l}^{-2}$.

Solubility of salts

Solubility (g per 100 g)

Ammonium acetate	253.2
Ammonium nitrate	389.6
Lithium nitrate	243.7
Sodium nitrate	97.6
Potassium nitrate	10.4
Sodium fluoride	0.35
Sodium chloride	3.0
Sodium bromide	138.0
Sodium iodide	161.9
Sodium thiocyanate	205.5

Liquid ammonia is an ionizing solvent, although less so than water, and dissolves a range of ionic compounds including many nitrates, nitrites, cyanides and thiocyanates. Most ammonium salts are soluble, and these salts act as acids in liquid ammonia solutions. The solubility of halide salts increases from fluoride to iodide. A saturated solution of ammonium nitrate contains 0.83 mol solute per mole of ammonia, and has a vapour pressure of less than 1 bar even at $25\text{ }^\circ\text{C}$.

Solutions of metals

See also: Solvated electron, metallic solution

Liquid ammonia will dissolve the alkali metals and other electropositive metals such as calcium, strontium, barium, europium and ytterbium. At low concentrations ($<0.06\text{ mol/L}$), deep blue solutions are formed: these contain metal cations and solvated electrons, free electrons which are surrounded by a cage of ammonia molecules.

These solutions are very useful as strong reducing agents. At higher concentrations, the solutions are metallic in appearance and in electrical conductivity. At low temperatures, the two types of solution can coexist as immiscible phases.

Redox properties of liquid ammonia

See also: Redox.

E° (V, ammonia) E° (V, water)

$\text{Li}^+ + \text{e}^- \rightleftharpoons \text{Li}$ -2.24 -3.04

$K^+ + e^- \rightleftharpoons K$	-1.98	-2.93
$Na^+ + e^- \rightleftharpoons Na$	-1.85	-2.71
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	-0.53	-0.76
$NH_4^+ + e^- \rightleftharpoons \frac{1}{2} H_2 + NH_3$	0.00	—
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.43	+0.34
$Ag^+ + e^- \rightleftharpoons Ag$	+0.83	+0.80

The range of thermodynamic stability of liquid ammonia solutions is very narrow, as the potential for oxidation to dinitrogen, E° ($N_2 + 6NH_4^+ + 6e^- \rightleftharpoons 8NH_3$), is only +0.04 V. In practice, both oxidation to dinitrogen and reduction to dihydrogen are slow. This is particularly true of reducing solutions: the solutions of the alkali metals mentioned above are stable for several days, slowly decomposing to the metal amide and dihydrogen. Most studies involving liquid ammonia solutions are done in reducing conditions: although oxidation of liquid ammonia is usually slow, there is still a risk of explosion, particularly if transition metal ions are present as possible catalysts.

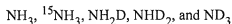
Detection and determination

Ammonia and ammonium salts can be readily detected, in very minute traces, by the addition of Nessler's solution, which gives a distinct yellow coloration in the presence of the least trace of ammonia or ammonium salts. Sulfur sticks are burnt to detect small leaks in industrial ammonia refrigeration systems. Larger quantities can be detected by warming the salts with a caustic alkali or with quicklime, when the characteristic smell of ammonia will be at once apparent. The amount of ammonia in ammonium salts can be estimated quantitatively by distillation of the salts with sodium or potassium hydroxide, the ammonia evolved being absorbed in a known volume of standard sulfuric acid and the excess of acid then determined volumetrically; or the ammonia may be absorbed in hydrochloric acid and the ammonium chloride so formed precipitated as ammonium hexachloroplatinate, $(NH_4)_2PtCl_6$.

Interstellar space

Ammonia was first detected in interstellar space in 1968, based on microwave emissions from the direction of the galactic core.^[16] This was the first polyatomic molecule to be so detected. The sensitivity of the molecule to a broad range of excitations and the ease with which it can be observed in a number of regions has made ammonia one of the most important molecules for studies of molecular clouds.^[17] The relative intensity of the ammonia lines can be used to measure the temperature of the emitting medium.

The following isotopic species of ammonia have been detected:



The detection of triply-deuterated ammonia was considered a surprise as deuterium is relatively scarce. It is thought that the low-temperature conditions allow this molecule to survive and accumulate.^[18] The ammonia molecule has also been detected in the atmospheres of the gas giant planets, including Jupiter, along with other gases like methane, hydrogen, and helium. The interior of Saturn may include frozen crystals of ammonia.^[19]

Safety precautions

Toxicity and storage information

The toxicity of ammonia solutions does not usually cause problems for humans and other mammals, as a specific mechanism exists to prevent its build-up in the bloodstream. Ammonia

is converted to carbamoyl phosphate by the enzyme carbamoyl phosphate synthase, and then enters the urea cycle to be either incorporated into amino acids or excreted in the urine. However fish and amphibians lack this mechanism, as they can usually eliminate ammonia from their bodies by direct excretion. Ammonia even at dilute concentrations is highly toxic to aquatic animals, and for this reason it is classified as *dangerous for the environment*. Ammonium compounds should never be allowed to come in contact with bases (unless an intended and contained reaction), as dangerous quantities of ammonia gas could be released.

Household use

Solutions of ammonia (5–10% by weight) are used as household cleaners, particularly for glass. These solutions are irritating to the eyes and mucous membranes (respiratory and digestive tracts), and to a lesser extent the skin. They should **never** be mixed with chlorine-containing products or strong oxidants, for example household bleach, as a variety of toxic and carcinogenic compounds are formed (e.g., chloramine, hydrazine, and chlorine gas).



Hydrochloric acid sample releasing HCl fumes which are reacting with ammonia fumes to produce a white smoke of ammonium chloride.

Laboratory use of ammonia solutions

The hazards of ammonia solutions depend on the concentration: "dilute" ammonia solutions are usually 5–10% by weight (<5.62 mol/L); "concentrated" solutions are usually prepared at >25% by weight. A 25% (by weight) solution has a density of 0.907 g/cm³, and a solution which has a lower density will be more concentrated. The European Union classification of ammonia solutions is given in the table.

Concentration by weight	Molarity	Classification	R-Phrases
5–10%	2.87–5.62 mol/L	Irritant (Xi)	R36/37/38
10–25%	5.62–13.29 mol/L	Corrosive (C)	R34
>25%	>13.29 mol/L	Corrosive (C) Dangerous for the environment (N)	R34, R50

S-Phrases: S1/2, S16, S36/37/39, S45, S61.

The ammonia vapour from concentrated ammonia solutions is severely irritating to the eyes and the respiratory tract, and these solutions should only be handled in a fume hood. Saturated ("0.880") solutions can develop a significant pressure inside a closed bottle in warm weather, and the bottle should be opened with care: this is not usually a problem for 25% ("0.900") solutions.

Ammonia solutions should not be mixed with halogens, as toxic and/or explosive products are formed. Prolonged contact of ammonia solutions with silver, mercury or iodide salts can also lead to explosive products: such mixtures are often formed in qualitative chemical analysis, and should be acidified and diluted before disposal once the test is completed.

Laboratory use of anhydrous ammonia (gas or liquid)

Anhydrous ammonia is classified as **toxic (T)** and **dangerous for the environment (N)**. The gas is flammable (autoignition temperature: 651 °C) and can form explosive mixtures with air (16–25%). The permissible exposure limit (PEL) in the United States is 50 ppm (35 mg/m³), while the IDLH concentration is estimated at 300 ppm. Repeated exposure to ammonia lowers the sensitivity to the smell of the gas: normally the odour is detectable at concentrations of less than 0.5 ppm, but desensitized individuals may not detect it even at concentrations of 100 ppm. Anhydrous ammonia corrodes copper- and zinc-containing alloys, and so brass fittings should not be used for handling the gas. Liquid ammonia can also attack rubber and certain plastics.

Ammonia reacts violently with the halogens, and causes the explosive polymerization of ethylene oxide. It also forms explosive compounds with compounds of gold, silver, mercury, germanium or tellurium, and with stibine. Violent reactions have also been

reported with acetaldehyde, hypochlorite solutions, potassium ferricyanide and peroxides.

See also

- Ammonia (data page)
- Ammonia production
- Chlorination
- Water purification

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External links

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- International Chemical Safety Card 0414 (http://www.ilo.org/public/english/protection/safework/cis/products/icsc/dtasht/_icsc04/icsc0414.htm) (anhydrous ammonia)
- International Chemical Safety Card 0215

(http://www.ilo.org/public/english/protection/safework/cis/products/icsc/dtasht/_icsc02/icsc0215.htm) (aqueous solutions)

- National Pollutant Inventory - Ammonia (<http://www.npi.gov.au/database/substance-info/profiles/8.html>)
- NIOSH Pocket Guide to Chemical Hazards (<http://www.cdc.gov/niosh/npg/npgd0028.html>)
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- CID 222 (<http://pubchem.ncbi.nlm.nih.gov/summary/summary.cgi?cid=222>) from PubChem
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- NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry/>)
- Computational Chemistry Wiki (<http://www.compchemwiki.org/index.php?title=Ammonia>)
- Link page to external chemical sources.

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Sodium

From Wikipedia, the free encyclopedia

For sodium in the diet, see Edible salt.

Sodium is the chemical element that has the symbol **Na** (*Natrium* in Latin) and atomic number 11. Sodium is a soft, waxy, silvery reactive metal belonging to the alkali metals that is abundant in natural compounds (especially halite). It is highly reactive, burns with a yellow flame, reacts violently with water and oxidizes in air necessitating storage in an inert environment.

Contents

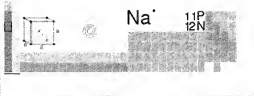
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Notable characteristics

Like the other alkali metals, sodium metal is a soft, light-weight, silvery white, reactive metal. Owing to its extreme reactivity, in nature it occurs only combined into compounds, and never as a pure elemental metal. Sodium metal floats on water, and reacts violently with it releasing heat, flammable hydrogen gas and caustic sodium hydroxide solution. Depending on the mass of sodium used and the amount of agitation, this reaction may be explosive.

Sodium ions are necessary for regulation of blood and body fluids, transmission of nerve impulses, heart activity, and certain metabolic functions. Interestingly, sodium is needed by animals, which maintain high concentrations in their blood and extracellular fluids, but the ion is not needed by plants. A completely plant-based diet, therefore, will be very low in sodium. This requires some herbivores to obtain their sodium from salt licks and other mineral sources. The animal need for sodium is probably the reason for the highly conserved ability to taste sodium ion, as "salty." Receptors for the salty taste respond best to sodium, and otherwise only to a few other small monovalent cations (Li^+ , NH_4^+ , and to some extent also K^+). Sodium salts without exception are soluble in water, and all of them are salty to the taste.

The most common sodium salt, sodium chloride (table salt), used for seasoning and food preservation, has been an important commodity in

11	neon ← sodium → magnesium
Li ↑ Na ↓ K	

General

Name, Symbol, Number	sodium, Na, 11
Chemical series	alkali metals
Group, Period, Block	1, 3, s

human activities (the English word *salar*y refers to *salar*ium, the perquisite given to Roman soldiers for the purpose of buying salt).

The human requirement for sodium in the diet is less than 500 mg per day, which is typically less than a tenth as much as many diets "seasoned to taste." Most people consume far more sodium than is physiologically needed. For certain people with salt-sensitive blood pressure, this extra intake may cause a negative effect on health. See edible salt.

Applications



Sodium in its metallic form can be used to refine some reactive metals, such as zirconium and potassium, from their compounds. This alkali metal as the Na⁺ ion is vital to animal life. Other uses:

In certain alloys to improve their structure.
In soap, in combination with fatty acids. Sodium soaps are harder

(higher melting) soaps than potassium soaps.

- To descale metal (make its surface smooth).
- To purify molten metals.
- In sodium vapor lamps, an efficient means of producing light from electricity (see the picture), often used for street lighting in cities. Low-pressure sodium lamps give a distinctive yellow-orange light which consists primarily of the twin sodium D spectral lines. High-pressure sodium lamps give a more natural peach-colored light, composed of wavelengths spread much more widely across the spectrum.
- As a heat transfer fluid in some types of nuclear reactors and inside the hollow valves of high-performance internal combustion engines.
- NaCl, a compound of sodium ions and chloride ions, is an important heat transfer material.
- In organic synthesis, sodium is used as a reducing agent, for example in the Birch reduction.
- In chemistry, sodium is often used either alone or with potassium in an alloy, NaK as a desiccant for drying solvents. Used with benzophenone, it forms an intense blue coloration when the solvent is dry and oxygen-free.

Oxidation states	1 (strongly basic oxide)
Electronegativity	0.93 (Pauling scale)
Ionization energies (more)	1st: 495.8 kJ·mol ^{−1}
	2nd: 4562 kJ·mol ^{−1}
	3rd: 6910.3 kJ·mol ^{−1}
Atomic radius	180 pm
Atomic radius (calc.)	190 pm
Covalent radius	154 pm
Van der Waals radius	227 pm

Miscellaneous	
Magnetic ordering	paramagnetic
Electrical resistivity	(20 °C) 47.7 nΩ·m
Thermal conductivity	(300 K) 142 W·m ^{−1} ·K ^{−1}
Thermal expansion	(25 °C) 71 μm·m ^{−1} ·K ^{−1}
Speed of sound (thin rod)	(20 °C) 3200 m/s
Young's modulus	10 GPa
Shear modulus	3.3 GPa
Bulk modulus	6.3 GPa
Mohs hardness	0.5
Brinell hardness	0.69 MPa
CAS registry number	7440-23-5

Notable isotopes					
Main article: Isotopes of sodium					
iso	NA	half-life	DM	DE (MeV)	DP
²² Na	syn	2.602 y	β ⁺	0.546	²² Ne
			ε	-	²² Ne
			γ	1.2745	-
²³ Na	100%	Na is stable with 12 neutrons			

References

History

Sodium (English, soda) has long been recognized in compounds, but was not isolated until 1807 by Sir Humphry Davy through the electrolysis of caustic soda. In medieval Europe a compound of sodium with the Latin name of *sodanum* was used as a headache remedy. Sodium's symbol, Na, comes from the neo-Latin name for a common sodium compound named *natrum*, which comes from the Greek *nitron*, a kind of natural salt. The difference between the English name, Soda, and the abbreviation, *Na* stems from Berzelius' publication of his system of atomic symbols in Thomas Thomson's Annals of Philosophy^[1].

Sodium imparts an intense yellow color to flames. As early as 1860 Kirchhoff and Bunsen noted the high sensitivity that a flame test for sodium could give. They state in Annalen der Physik und der Chemie in the paper "Chemical Analysis by Observation of

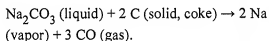
In a corner of our 60 cu.m. room farthest away from the apparatus, we exploded 3 mg. of sodium chlorate with milk sugar while observing the nonluminous flame before the slit. After a few minutes, the flame gradually turned yellow and showed a strong sodium line that disappeared only after 10 minutes. From the weight of the sodium salt and the volume of air in the room, we easily calculate that one part by weight of air could not contain more than 1/20 millionth weight of sodium.

Occurrence

See also sodium minerals.

Sodium is relatively abundant in stars and the D spectral lines of this element are among the most prominent in star light. Sodium makes up about 2.6% by weight of the Earth's crust making it the fourth most abundant element overall and the most abundant alkali metal.

At the end of the 19th century, sodium was chemically prepared by heating sodium carbonate with carbon at 1100 °C.



It is now produced commercially through the electrolysis of liquid sodium chloride. This is done in a Down's cell in which the NaCl is mixed with calcium chloride to lower the melting point below 700 °C. As calcium is more electropositive than sodium, no calcium will be formed at the cathode. This method is less expensive than the previous method of electrolyzing sodium hydroxide.

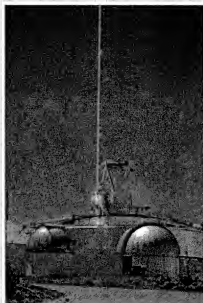
Metallic sodium cost about 15 to 20 US cents per pound (US\$0.30/kg to US\$0.45/kg) in 1997 but reagent grade (ACS) sodium cost about US\$35 per pound (US\$75/kg) in 1990.

Phase behavior under pressure

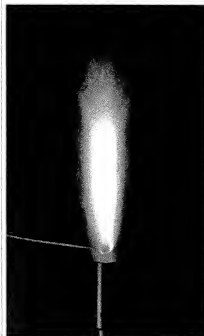
Under extreme pressure, sodium departs from common melting behavior. Most materials require higher temperatures to melt under pressure than they do at normal atmospheric pressure. This is because they expand on melting due to looser molecular packing in the liquid, and thus pressure forces equilibrium in the direction of the denser solid phase.

At a pressure of 30 gigapascals (300,000 times sea level atmospheric pressure), the melting temperature of sodium begins to drop. At around 100 gigapascals, sodium will melt at near room temperature. A possible explanation for the aberrant behavior of sodium is that this element has one free electron that is pushed closer to the other 10 electrons when placed under pressure, forcing interactions that are not normally present. While under pressure, solid sodium assumes several odd crystal structures suggesting that the liquid might have unusual properties such as superconduction or superfluidity. (Gregoryanz, *et al.*, 2005)

Compounds



A dye laser used at the Starfire Optical Range for LIDAR and laser guide star experiments is tuned to the sodium D line and used to excite sodium atoms in the upper atmosphere.



The flame test for sodium displays a brilliantly bright yellow emission due to the so called "sodium D-lines" at 588.9950 and 589.5924 nanometers.

See also sodium compounds.

Sodium chloride or halite, better known as common salt, is the most common compound of sodium, but sodium occurs in many other minerals, such as amphibole, cryolite, soda niter and zeolite. Sodium compounds are important to the chemical, glass, metal, paper, petroleum, soap, and textile industries. Hard soaps are generally sodium salt of certain fatty acids (potassium produces softer or liquid soaps).

The sodium compounds that are the most important to industry are common salt (NaCl), soda ash (Na_2CO_3), baking soda (NaHCO_3), caustic soda (NaOH), Chile saltpeter (NaNO_3), di- and tri-sodium phosphates, sodium thiosulfate (hypo, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), and borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$).

Isotopes

There are thirteen isotopes of sodium that have been recognized. The only stable isotope is ^{23}Na . Sodium has two radioactive cosmogenic isotopes (^{22}Na , half-life = 2.605 years; and ^{24}Na , half-life \approx 15 hours).

Acute neutron radiation exposure (e.g., from a nuclear criticality accident) converts some of the stable ^{23}Na in human blood plasma to ^{24}Na . By measuring the concentration of this isotope, the neutron radiation dosage to the victim can be computed.

Precautions

Extreme care is required in handling elemental/metallic sodium. Sodium is potentially explosive in water (depending on quantity) and is a caustic poison, since it is rapidly converted to sodium hydroxide on contact with moisture. The powdered form may combust spontaneously in air or oxygen. Sodium must be stored either in an inert (oxygen and moisture free) atmosphere (such as nitrogen or argon), or under a liquid hydrocarbon such as mineral oil or kerosene.

The reaction of sodium and water is a familiar one in chemistry labs, and is reasonably safe if amounts of sodium smaller than a pencil eraser are used, and the reaction is done behind a plastic shield glass by people wearing eye protection. However, the sodium-water reaction does not scale up well, and is treacherous when larger amounts of sodium are used. Larger pieces of sodium melt under the heat of the reaction, and the molten ball of metal is buoyed up by hydrogen and may appear to be stably reacting with water, until splashing covers more of the reaction mass, causing thermal runaway and an explosion which scatters molten sodium metal, lye solution, and sometimes flame. This behavior is unpredictable, and among the alkali metals it is usually sodium which invites this surprise phenomenon, because lithium is not reactive enough to do it, and potassium is so reactive that chemistry students are not tempted to try the reaction with larger potassium pieces.

Sodium is much more reactive than magnesium. When the metal itself catches fire (as opposed to just the hydrogen gas generated from it) it burns at high temperatures and also melts, which spreads the flame and exposes even more surface area to the air.

Few common fire extinguishers work on sodium fires. Water, of course, exacerbates sodium fires, as do water-based foams. CO_2 and Halon are often ineffective on sodium fires, which reignite when the extinguisher dissipates. Among the very few materials effective on a sodium metal fire are Pyromet and Met-L-X. Pyromet is a $\text{NaCl}/(\text{NH}_4)_2\text{HPO}_4$ mix, with flow/anti-clump agents. It smothers the fire, drains away heat, and melts to form an impermeable crust. This is the standard dry-powder canister fire extinguisher for all classes of fires. Met-L-X is mostly sodium chloride, NaCl, with approximately 5% Saran plastic as a crust-former, and flow/anti-clumping agents. It is most commonly hand-applied, with a scoop. Other extreme fire extinguishing materials include Lith-X, a graphite based dry powder with an organophosphate flame retardant; and Na-X, a Na_2CO_3 -based material.

Because of the reaction scale problems discussed above, disposing of large quantities of sodium (more than 10 to 100 grams) must be done through a licensed hazardous materials disposer. Smaller quantities may be broken up and neutralized carefully with ethanol (which has a much slower reaction than water), or even methanol (where the reaction is more rapid), but care should nevertheless be taken, as the caustic products from the ethanol or methanol reaction are just as hazardous to eyes and skin as those from water. After the alcohol reaction appears complete and all pieces of reaction debris have been broken up or dissolved, a mixture of alcohol and water, then pure water, may then be carefully used for a final cleaning. This should be allowed to stand a

few minutes before the reaction products are diluted more thoroughly and flushed down the drain. The purpose of the final water soak and wash of any reaction mass which may contain sodium, is to ensure that alcohol does not carry unreacted sodium into the sink trap, where a water reaction may generate hydrogen in the trap space which can then be potentially ignited, causing a confined sink trap explosion.

Physiology and sodium ions

Sodium ions play a diverse and important role in many physiological processes. Excitable animal cells, for example, rely on the entry of Na^+ to cause a depolarization. An example of this is signal transduction in the human central nervous system, which depends on sodium ion motion in all nerves.

Some potent neurotoxins, such as batrachotoxin, increase the sodium ion permeability of the cell membranes in nerves and muscles, causing a massive and irreversible depolarization of the membranes, with potentially fatal consequences. However, drugs with smaller effects on sodium ion motion in nerves may have diverse pharmacological effects which range from anti-depressant to anti-seizure actions.

Sodium is the primary cation (positive ion) in extracellular fluids in animals and humans. These fluids, such as blood plasma and extracellular fluids in other tissues, bathe cells and carry out transport functions for nutrients and wastes. Sodium is also the principal cation in seawater, although the concentration there is about three times what it is normally in extracellular body fluids. This suggests that animal life moved from the sea to dry land at a time when the seas were far less salty than they are now.

Although the system for maintaining optimal salt and water balance in the body is a complex one, one of the primary ways in which the human body keeps track of loss of body water is that osmoreceptors in the hypothalamus sense a balance of sodium and water concentration in extracellular fluids. Relative loss of body water will cause sodium concentration to rise higher than normal, a condition known as hypernatremia. This ordinarily results in thirst. Conversely, an excess of body water caused by drinking will result in too little sodium in the blood (hyponatremia), a condition which is again sensed by the hypothalamus, causing a decrease in vasopressin hormone secretion from the posterior pituitary, and a consequent loss of water in the urine, which acts to restore blood sodium concentrations to normal.

Severely dehydrated persons, such as people rescued from ocean or desert survival situations, usually have very high blood sodium concentrations. These must be very carefully and slowly returned to normal, since too-rapid correction of hyponatremia may result in brain damage from cellular swelling as water moves suddenly into cells with high osmolar content.

Because the hypothalamus/osmoreceptor system ordinarily works well to cause drinking or urination to restore the body's sodium concentrations to normal, this system can be used in medical treatment to regulate the body's total fluid content by controlling the body's sodium content. Thus, when a powerful diuretic drug is given which causes the kidneys to excrete sodium, the effect is usually followed by an excretion of body water, as the osmoreceptor system senses the sodium loss, and then directs compensatory urinary loss of water in order to correct the hyponatremia, or (low-blood-sodium) state.

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See also



- Category:Sodium compounds
- Category:Alkali metals

External links

- WebElements.com – Sodium (<http://www.webelements.com/webelements/elements/text/Na/index.html>)
- The Wooden Periodic Table Table's Entry on Sodium (<http://www.theodoregray.com/PeriodicTable/Elements/011/index.html>)
- Dietary Sodium (<http://www.americanheart.org/presenter.jhtml?identifier=4708>)
- Link page to external chemical sources.

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Solution

From Wikipedia, the free encyclopedia
(Redirected from Solutions)

This article is about a chemical solution; for other uses of the term "solution", see solution (disambiguation)

In chemistry, a **solution** is a homogeneous mixture composed of one or more substances, known as **solutes**, dissolved in another substance, known as a solvent. A common example is a solid, such as salt or sugar, dissolved in water, a liquid. Gases may dissolve in liquids, for example, carbon dioxide or oxygen in water. Liquids may dissolve in other liquids and gases in other gases.

Examples of solid solutions are alloys and certain minerals.

Contents

- 1 Ideal solutions
- 2 Solvents
- 3 Solvation
- 4 Concentration
- 5 Types of solutions
- 6 References
- 7 See also

Ideal solutions

An **ideal solution** is one where the interactions of the molecules of the solvent with each other are equal to their interactions with the solutes. The properties of an ideal solution can be calculated by the linear combination of the properties of its components.

The solvent is conventionally defined as the substance that exists in a greater quantity than the solute(s) in the solution. If both solute and solvent exist in equal quantities (such as in a 50% ethanol, 50% water solution), the concepts of "solute" and "solvent" become less relevant, but the substance that is more often used as a solvent is normally designated as the solvent (in this example, water).

Solvents

Solvents can be broadly classified into polar and non-polar solvents. A common measure of the polarity of a solvent is the dielectric constant. The most widely used polar solvent is water, with a dielectric constant of 78.5. Ethanol, with a dielectric constant of 24.3, has intermediate polarity. An example of a non-polar solvent is hexane, which has a dielectric constant of 1.9. Generally polar or ionic compounds will only dissolve in polar solvents. A simple test for the polarity of a liquid solvent is to rub a plastic rod, to induce static electricity. Then hold this charged rod close to a running stream of the solvent. If the path of the solvent deviates when the rod is held close to it, it is a polar solvent. Certain molecules have polar and non-polar regions, for example sodium dodecyl sulfate. This class of molecules (called amphipathic molecules) includes surfactants like soaps and emulsifiers, as they have the ability to stabilize emulsions by aligning themselves on the interface between the non-polar and polar liquids, with their polar ends in the polar liquid and their non-polar ends in the non-polar liquid.

Solvation

During solvation, especially when the solvent is polar, a structure forms around it, which allows the solute-solvent interaction to



Dissolving table salt in water

remain stable.

When no more of a solute can be dissolved into a solvent, the solution is said to be saturated. However, the point at which a solution can become saturated changes significantly with different environmental factors, such as temperature, pressure, and contamination. Raising the solubility (for example by increasing the temperature) to dissolve more solute, and then lowering the solubility causes a solution to become supersaturated.

In general the greater the temperature of a solvent, the more of a given solid solute it can dissolve. However, some compounds exhibit reverse solubility, which means that as a solvent gets warmer, less solute can be dissolved. Some surfactants exhibit this behaviour. The solubility of liquids in liquids is generally less temperature-sensitive than that of solids or gases, while gases usually become less soluble with increasing temperature.

Concentration

There are several ways to measure the strength of a solution; see concentration for more information. Total dissolved solids is a common term in a range of disciplines, and can have different meanings depending on the analytical method used. In water quality, it refers to the amount of residue remaining after evaporation of water from a sample.

Types of solutions

Examples of solutions		Solute		
		Gas	Liquid	Solid
Solvent	Gas	Oxygen and other gases in nitrogen (air)	Water vapor in air (humidity)	The odor of a solid results from molecules of that solid being dissolved in the air
	Liquid	Carbon dioxide in water (carbonated water)	Ethanol (common alcohol) in water; various hydrocarbons in each other (petroleum)	Sucrose (table sugar) in water; sodium chloride (table salt) in water; gold in mercury, forming an amalgam
	Solid	Hydrogen dissolves rather well in metals; platinum has been studied as a storage medium	Water in activated charcoal; moisture in wood	Steel, duralumin, other metal alloys

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Streitwieser, Andrew; Heathcock, Clayton H., Kosower, Edward M. (1992). *Introduction to Organic Chemistry*, 4th ed., Macmillan Publishing Company, New York. ISBN 0-02-418170-6.

See also

- Colligative properties
- Colloid
- Molar solution
- Percentage solution
- Solubility equilibrium
- Solubility
- Suspension (chemistry)

Retrieved from "http://en.wikipedia.org/wiki/Solution"

Categories: Solutions | Homogeneous mixtures | Alchemical processes

	Look up <i>solution</i> in Wiktionary, the free dictionary.
	
	Look up <i>solute</i> in Wiktionary, the free dictionary.
	

Wikibooks has a book on the topic of *Transwiki:Creating chemical solutions*



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Sodium amide

From Wikipedia, the free encyclopedia

Sodium amide, also called **sodamide**, is NaNH_2 . This solid is highly reactive, dangerously so in the presence of moisture or air. It hydrolyzes readily to ammonia. The pure solid is white, but commercial samples are often grey in colour due to the presence of small quantities of metallic iron from the manufacturing process: this does not usually affect the use of the product. Sodium amide samples which are yellow or brown in colour should be destroyed immediately (see Safety below).

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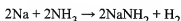
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Preparation

Sodium amide can be prepared by the reaction of sodium with ammonia gas.^[1]

(http://en.wikipedia.org/wiki/Sodium_amide#endnote_PrepnOS) but it is usually prepared by the reaction in liquid ammonia using iron (III) nitrate as a catalyst.^[2]

(http://en.wikipedia.org/wiki/Sodium_amide#endnote_PrepnIS)



Uses

Sodium amide is used in the industrial production of indigo, hydrazine, and sodium cyanide.^[3]

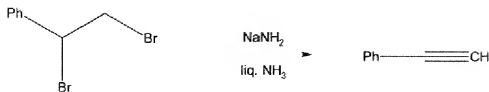
(http://en.wikipedia.org/wiki/Sodium_amide#endnote_Merck) It is the reagent of choice for the drying of ammonia (liquid or gaseous) and is also widely used as a strong base in organic chemistry, often in liquid ammonia solution. Its use has been superseded by the popularization of related reagents such as NaH , $\text{Na}[\text{Si}(\text{CH}_3)_2]$, and $\text{Li}[\text{CH}(\text{CH}_3)_2]$.

Preparation of alkynes

Sodium amide induces the loss of two molecules of hydrogen bromide from a vicinal dibromoalkane to give a

Sodium amide	
Image:Sodium amide.jpg	
General	
Other names	Sodamide
Molecular formula	NaNH_2
Molar mass	39.01 g/mol
Appearance	gray powder
CAS number	[7782-92-5]
Properties	
Density and phase	? g/cm ³ , ?
Solubility in water	reacts
Melting point	210°C
Boiling point	400°C
Basicity (p <i>K</i> _b)	≈19
Structure	
Coordination geometry	?
Crystal structure	?
Hazards	
MSDS	External MSDS
EU classification	not listed
NFPA 704	
Flash point	Non-flammable.
RTECS number	?
Supplementary data page	
Structure and properties	<i>n</i> , <i>ε</i> , etc.
Thermodynamic data	Phase behaviour Solid, liquid, gas
Spectral data	UV, IR, NMR, MS
Related compounds	
Other anions	Sodium hydroxide
Other cations	Potassium amide
Related compounds	Ammonia
Except where noted otherwise, data are given for materials in their standard state (at 25 °C, 100 kPa)	
Infobox disclaimer and references	

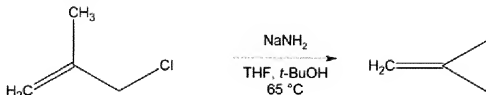
carbon-carbon triple bond, as in the preparation of phenylacetylene below.^[4]
(http://en.wikipedia.org/wiki/Sodium_amide#endnote_Campbell)



Hydrogen chloride and/or ethanol can also be eliminated in this way.^[5]
(http://en.wikipedia.org/wiki/Sodium_amide#endnote_Jones)[6] (http://en.wikipedia.org/wiki/Sodium_amide#endnote_Bou)[7]
(http://en.wikipedia.org/wiki/Sodium_amide#endnote_Magriotis)[8] (http://en.wikipedia.org/wiki/Sodium_amide#endnote_Ashworth)
as in the preparation of 1-ethoxy-1-butyne.^[9] (http://en.wikipedia.org/wiki/Sodium_amide#endnote_Newman)

Cyclization reactions

Where there is no β -hydrogen to be eliminated, cyclic compounds may be formed, as in the preparation of methylenecyclopropane below.^[10] (http://en.wikipedia.org/wiki/Sodium_amide#endnote_Salaun)



Cyclopropenes^[11] (http://en.wikipedia.org/wiki/Sodium_amide#endnote_Nakamura) aziridines^[12]
(http://en.wikipedia.org/wiki/Sodium_amide#endnote_Bottini) and cyclobutanes^[13]
(http://en.wikipedia.org/wiki/Sodium_amide#endnote_Skorez) may be formed in a similar manner.

Deprotonation of carbon and nitrogen acids

Carbon acids which can be deprotonated by sodium amide in liquid ammonia include terminal alkynes,^[14]
(http://en.wikipedia.org/wiki/Sodium_amide#endnote_Saunders)[15] (http://en.wikipedia.org/wiki/Sodium_amide#endnote_Peterson)
[16] (http://en.wikipedia.org/wiki/Sodium_amide#endnote_Kauer) methyl ketones,^[17]
(http://en.wikipedia.org/wiki/Sodium_amide#endnote_Coffman)[18] (http://en.wikipedia.org/wiki/Sodium_amide#endnote_Hauser2)
cyclohexanone,^[19] (http://en.wikipedia.org/wiki/Sodium_amide#endnote_Vanderwerf) phenylacetic acid and its derivatives
[20] (http://en.wikipedia.org/wiki/Sodium_amide#endnote_Hauser1)[21] (http://en.wikipedia.org/wiki/Sodium_amide#endnote_Kaiser)
[22] (http://en.wikipedia.org/wiki/Sodium_amide#endnote_Wawzonek) and diphenylmethane.^[23]
(http://en.wikipedia.org/wiki/Sodium_amide#endnote_Murphy) Acetylacetone loses two protons to form a dianion.^[24]
(http://en.wikipedia.org/wiki/Sodium_amide#endnote_Hampton)

Sodium amide will also deprotonate indole^[25] (http://en.wikipedia.org/wiki/Sodium_amide#endnote_Potts) and piperidine.
[26] (http://en.wikipedia.org/wiki/Sodium_amide#endnote_Bunnett)

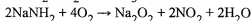
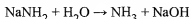
Other reactions

- Rearrangement with orthodeprotonation^[27] (http://en.wikipedia.org/wiki/Sodium_amide#endnote_Brasen)

- Oxirane synthesis (by carbene reaction?)^[28] (http://en.wikipedia.org/wiki/Sodium_amide#endnote_Allen1)
- Indole synthesis^[29] (http://en.wikipedia.org/wiki/Sodium_amide#endnote_Allen2)

Safety

Sodium amide reacts violently with water to produce ammonia and sodium hydroxide: and will burn in air to give oxides of sodium and nitrogen.



In the presence of limited quantities of air and moisture, such as in a poorly closed container, explosive mixtures of oxidation products can form. This is accompanied by a yellowing or browning of the solid. As such, sodium amide should always be stored in a tightly closed container, if possible under an atmosphere of nitrogen gas. Sodium amide samples which are yellow or brown in colour should be destroyed immediately: one method for destruction is the careful addition of ethanol to a suspension of sodium amide in a hydrocarbon solvent.

Sodium amide may be expected to be corrosive to the skin, eyes and mucous membranes. Care should be taken to avoid dispersal of the dust.

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External links

- Sodium amide reactions (http://www.orgsyn.org/orgsyn/default.asp?formgroup=basenp_form_group&dataaction=db&dbname=orgsyn) (from *Organic Syntheses*)
- Link page to external chemical sources.

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Categories: Sodium compounds | Amides

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CRC Handbook of Chem.
 & Physics, 73rd, 1992-93

PHYSICAL CONSTANTS OF INORGANIC COMPOUNDS (continued)

No.	Name	Synonyms and Formulae	Mol. wt.	Crystalline form, properties and index of refraction	Density or spec. gravity	Melting point, °C	Boiling point, °C	Solubility, in grams per 100 cc		
								Cold water	Hot water	Other solvents
1206	aluminum oriko-silicate	Nat. nephelite. $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	284.11	col. hex. 1.537 ± 0.002	2.619 ²¹	1526		i	d	d s
1207	aluminum sulfate	$\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	458.27	col. cub. oct. 1.4388	1.6754 ²⁰	61		110 ¹⁵ d (anhyd)	146 ²⁰ d (anhyd)	
1208	amide	Sodamide. NaNH_2	39.01	wh. conchoid fract. col. monoc. 1.439	1.554	210 d 79	400			d hex. al. 0.1 liq NH_3 i al. acet
1209	ammonium phosphate	Microcosmic salt, sarcosite. $\text{NaNH}_4\text{H}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$	209.07	wh. rhomb. 1.441, 1.469	1.631 ¹⁵	4 80		16.7	100	
1210	ammonium sulfate	$\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$	173.12	wh. rhomb. 1.590	1.590	21.09 ⁰				
1211	ammonium tetrathionate	$\text{Na}_2\text{S}_4\text{O}_{10} \cdot 4\text{H}_2\text{O}$	361.16	wh. powder 1.527				0.03-0.13	0.3-100	
1212	arsenite	Leucosmine. NaAsO_2	192.74	wh. powder 1.527						s Na_2S sol sl s al
1213	arsenite, hydroxy	"Pyroantimonite". $\text{NaSb}(\text{OH})_4$	246.78	wh. powder 1.527						
1214	pyroantimonite, dihydro-antimonide	$\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7 \cdot \text{H}_2\text{O}$	511.58	wh. tetrag. 1.466		d 280				
1215	arsenite	NaAsO_2	190.72	wh. powder or bl. cr. inflamm.		856			0.28 ¹⁰⁰	d
1216	arsenite	$\text{NaAsO}_2 \cdot 2\text{H}_2\text{O}$	230.78	col. rhomb. 1.479	2.864					d s NH_3
1217	arsenite	NaAsO_2	145.91	col. rhomb. 1.479	2.301	615		v s		
1218	orthoarsenate	$\text{Na}_2\text{AsO}_4 \cdot 12\text{H}_2\text{O}$	424.07	col. trig. or hex. prism. 1.457, 1.466	1.752-1.804	86.3		38.9 ¹⁵		1.67 al; 50 ¹⁵ glye
1219	orthoarsenate, di-H	$\text{NaH}_2\text{AsO}_4 \cdot \text{H}_2\text{O}$	181.94	col. rhomb. or monoc. 1.583, 1.553, 1.507	2.53	130, - H_2O 100	d 200-280	s		
1220	orthoarsenate, mono-H	$\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$	312.01	col. monoc. 1.462, 1.466, 1.478	1.88	130, - H_2O 50	d 180	5.46 ⁰	100 ¹⁰⁰	s glye; sl s al
1221	orthoarsenate, mono-H	$\text{NaH}(\text{AsO}_4) \cdot 12\text{H}_2\text{O}$	402.09	col. monoc. eff. 1.445, 1.466, 1.451	1.736	28	-12 H_2O , 100	56 ¹⁴	140.7 ¹⁰	d al; i liq Cl
1222	pyroarsenate	$\text{Na}_4\text{As}_2\text{O}_7$	353.80	wh. cr. 1.465, 1.467, 1.469	2.205, 2.849 ¹⁵	850	d 1000	v s		
1223	arsenate fluoride	$2\text{Na}_2\text{AsO}_4 \cdot \text{NaF} \cdot 19\text{H}_2\text{O}$	800.06	gray-wh. powder, pois.	1.87			v s		sl s al
1224	arsenite	Sodium metaarsenite (?) (com'l) NaAsO_2 for mix with Na_2AsO_4	129.91	gray-wh. powder, pois.	1.87			v s		sl s al
1225	arsenotetratrate	$\text{Na}(\text{AsO})_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$	307.02	shiny cr. pois.		-2 H_2O , 275 d Na + N	d 275	6.5 ¹⁵		i al
1226	arside	NaH_2	65.01	col. hex. 1.846 ²⁰						
1227	hebsial	$\text{Na}_2\text{C}_4\text{H}_4\text{N}_2\text{O}_6$	206.18	wh. powder				20 ¹⁵	40 ¹⁰⁰	0.314 ¹⁴ al; s liq NH_3 , i eth sl s al; i eth
1228	benzenesulfonate	$\text{NaC}_6\text{H}_5\text{SO}_3$	180.15	wh. cr.				35.8 ¹⁰	74.2 ¹⁰⁰	1.64 ¹⁵ al
1229	benzoate	$\text{NaC}_6\text{H}_5\text{O}_2$	144.11	col. cr. or wh. amorph. or gran. powder				66 ²⁰		
1230	metaborismate	NaBO_3	297.97	yellow powder (com'l), yell. (pure)						d a
1231	metaborate	NaBO_2	65.80	col. hex. pr. 1.466	2.464	966	1434	26 ²⁰	36 ¹⁵	
1232	metaborate, tetrahydrate	$\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$	127.86	trich. col. monoc. 1.439	1.57	57	- H_2O , 120	v s		
1233	metaborate, peroxyhydrate	Sodium perborate (com'l). $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$	153.86	col. monoc. 1.439	1.57	57	- H_2O , 130	2.55 ¹⁵	3.75 ¹⁵	s a, al. glye
1234	metaborate	NaBO_2	65.80	wh. powder				150		
1235	metaborate, decalhydrate	Borax. $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	201.22	cr. 1.5010	2.367	741	d 1575	1.00 ⁰	8.79 ¹⁰	i al
1236	metaborate, pentahydrate	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$	381.37	col. monoc. eff. 1.447, 1.469, 1.472	1.73	75, - H_2O , 60	-10 H_2O , 320	2.0 ¹⁰	170 ¹⁰⁰	v s al; s glye; i a
1237	borohydride	NaBH_4	37.83	col. cub. or hex. deliq. 1.461	1.815		- H_2O , 120	22.6 ¹⁰	52.3 ¹⁰⁰	
1238	borate	NaBrO_3	150.89	col. cub. 1.594	3.339 ^{17,18}	381		55 ¹⁰		4 al; 16.4 MeOH; s pyr; i eth
1239	borate	NaBr	102.89	col. cub. 1.594	3.339 ^{17,18}	747		27.5 ¹⁰	90.9 ¹⁰⁰	i al
1240	borate, dihydrate	$\text{NaBr} \cdot 2\text{H}_2\text{O}$	138.92	col. monoc. pr. 1.6412	2.203 ¹⁷	747	1390	121 ¹⁰⁰		sl s al
1241	metaborate	$\text{NaAuBr}_2 \cdot 2\text{H}_2\text{O}$	575.60	br. blk. cr.	2.176		-2 H_2O , 51	79.5 ⁰	118.6 ¹⁰	2.31 ¹⁵ al; s liq NH_3 , 17.42 ¹⁵ MeOH
1242	metaborate	$\text{Na}_3\text{HfBr}_4 \cdot 12\text{H}_2\text{O}$	956.80	dk. gm. rhomb. eff.		100	- H_2O , 130	s		s NH_4OH
1243	metaborate	$\text{Na}_3\text{HfBr}_4 \cdot 6\text{H}_2\text{O}$	828.58	dk. red. trich. 1.323		d 150		v s		v s al
1244	metaborate	$\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$	214.03	wh.		ea 60	- H_2O , 120	200 ¹⁵⁻²⁰		40 ¹⁵ al; 100 ¹⁵⁻²⁰ 90% al
1245	calcium sulfate	$\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{SO}_4 \cdot 2\text{H}_2\text{O}$	314.21	col. monoc. need.	2.64		-2 H_2O , 80			d
1246	calcium phosphate	$\text{Na}_2\text{C}_2\text{O}_4 \cdot \text{Ca}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$	298.24	wh. need. hygr.			-3 H_2O , 100	122 ¹⁴		s al
1247	calcide	$\text{Na}_2\text{C}_2\text{O}_4$	70.00	wh. powder 1.575 ¹⁵		ea 700		7.1 ¹⁰	45.5 ¹⁰⁰	s; d al sl s abs. al; i acet
1248	calcane	Na_2CO_3	105.99	wh. powder, hygr. 1.535	2.532	851				
1249	carbonate, decahydrate	Washing soda. $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	286.14	wh. monoc. 1.405, 1.425, 1.440	1.44 ¹⁵	32.5-34.5	- H_2O , 33.5	21.5 ¹⁰	421 ¹⁰⁴	i al
1250	carbonate, heptahydrate	$\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$	232.10	rhomb. bihydr. eff.	1.51		- H_2O , 32	16.90	33.9 ¹⁵	
1251	carbonate, monohydrate	Crystal carbonate, thermantite. $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	124.00	col. rhomb. deliq. 1.506, 1.509	2.25		- H_2O , 100	52.08	14 ¹⁵ glye; i al, eth	

SODIUM AND SODIUM ALLOYS

SODIUM

Sodium [7440-23-5], Na, an alkali metal, is the second element of Group 1 (IA) of the Periodic Table, atomic wt 22.9898. The chemical symbol is derived from the Latin *natrium*. Commercial interest in the metal derives from its high chemical reactivity, low melting point, high boiling point, good thermal and electrical conductivity, and high value in use.

Sir Humphry Davy first isolated metallic sodium in 1807 by the electrolytic decomposition of sodium hydroxide. Later, the metal was produced experimentally by thermal reduction of the hydroxide with iron. In 1855, commercial production was started using the Deville process, in which sodium carbonate was reduced with carbon at 1100°C. In 1886 a process for the thermal reduction of sodium hydroxide with carbon was developed. Later sodium was made on a commercial scale by the electrolysis of sodium hydroxide (1,2). The process for the electrolytic decomposition of fused sodium chloride, patented in 1924 (2,3), has been the preferred process since installation of the first electrolysis cells at Niagara Falls in 1925. Sodium chloride decomposition is widely used throughout the world (see SODIUM COMPOUNDS).

Sodium was first used commercially to make aluminum by reduction of sodium aluminum chloride. The principal application as of the mid-1990s is for the manufacture of tetraethyllead (TEL), the antiknock gasoline additive. However, TEL use is declining worldwide because of the recognized toxic effects of lead (qv) released to the environment (see LEAD COMPOUNDS, INDUSTRIAL TOXICOLOGY). Sodium use is growing for manufacture of sodium borohydride and agricultural crop protection chemicals (see BORON COMPOUNDS; FUNGICIDES, AGRICULTURAL). Smaller amounts of sodium are used to produce sodium hydride, indigo dyes, tantalum metal powders, silicon, and sodium peroxide; in the preparation of many organic compounds, pharmaceuticals (qv), sodium azide, and copper; and in lead dross refining.

Sodium is not found in the free state in nature because of its high chemical reactivity. It occurs naturally as a component of many complex minerals and of such simple ones as sodium chloride, sodium carbonate, sodium sulfate, sodium borate, and sodium nitrate. Soluble sodium salts are found in seawater, mineral springs, and salt lakes. Principal U.S. commercial deposits of sodium salts are the Great Salt Lake, Searles Lake, and the rock salt beds of the Gulf Coast, Virginia, New York, and Michigan (see CHEMICALS FROM BRINE). Sodium-23 is the only naturally occurring isotope. The six artificial radioisotopes (qv) are listed in Table 1 (see SODIUM COMPOUNDS).

Physical Properties

Sodium is a soft, malleable solid readily cut with a knife or extruded as wire. It is commonly coated with a layer of white sodium monoxide, carbonate, or hydroxide, depending on the degree and kind of atmospheric exposure. In a

Table 1. Radioisotopes of Sodium

Isotope	CAS Registry Number	Half-life, s
sodium-20	[14809-59-7]	0.4
sodium-21	[15594-24-8]	23.0
sodium-22	[13966-32-0]	2.58 ^a
sodium-24	[13982-04-2]	15.0 ^p
sodium-25	[15760-13-1]	60.0
sodium-26	[26103-12-8]	1.0

^a Expressed in years.^p Expressed in hours.

strictly anhydrous inert atmosphere, the freshly cut surface has a faintly pink, bright metallic luster. Liquid sodium in such an atmosphere looks much like mercury. Both liquid and solid oxidize in air, but traces of moisture appear to be required for the reaction to proceed. Oxidation of the liquid is accelerated by an increase in temperature, or by increased velocity of sodium through an air or oxygen environment.

Only body-centered cubic crystals, lattice constant 428.2 pm at 20°C, are reported for sodium (4). The atomic radius is 185 pm, the ionic radius 97 pm, and electronic configuration is $1s^2s^22p^63s^1$ (5). Physical properties of sodium are given in Table 2. Greater detail and other properties are also available (5).

Sodium is paramagnetic. The vapor is chiefly monatomic, although the dimer and tetramer have been reported (6). Thin films are opaque in the visible range but transmit in the ultraviolet at ca 210 nm. The vapor is blue, but brilliant green is frequently observed when working with sodium at high temperature, presumably because of mixing of the blue with yellow from partial burning of the vapor.

At 100–300°C sodium readily wets and spreads over many dry solids, eg, sodium chloride or aluminum oxide. In this form the metal is highly reactive (7), but it does not easily wet stainless or carbon steels. Wetting of structural metals is influenced by the cleanliness of the surface, the purity of the sodium, temperature, and the time of exposure. Wetting occurs more readily at $\geq 300^\circ\text{C}$ and, once attained, persists at lower temperatures (5).

Sodium Dispersions. Sodium is easily dispersed in inert hydrocarbons (qv), eg, white oil or kerosene, by agitation, or using a homogenizing device. Addition of oleic acid and other long-chain fatty acids, higher alcohols and esters, and some finely divided solids, eg, carbon or bentonite, accelerate dispersion and produce finer (1–20 μm) particles. Above 98°C the sodium is present as liquid spheres. On cooling to lower temperatures, solid spheres of sodium remain dispersed in the hydrocarbon and present an extended surface for reaction. Dispersions may contain as much as 50 wt % sodium. Sodium in this form is easily handled and reacts rapidly. For some purposes the presence of the inert hydrocarbon is a disadvantage.

High Surface Sodium. Liquid sodium readily wets many solid surfaces. This property may be used to provide a highly reactive form of sodium without contamination by hydrocarbons. Powdered solids having a high surface area per unit volume, eg, completely dehydrated activated alumina powder, provide

Table 2. Physical Properties of Sodium^a

Property	Value	Property	Value
ionization potential, V	5.12	specific heat, kJ/(kg·K) ^b	
melting point, °C	97.82	solid	
heat of fusion, kJ/kg ^b	113	at 20°C	2.01
volume change on melting, %	2.63	mp	2.16
boiling point, °C	881.4	liquid	
heat of vaporization	3.874	at mp	1.38
at bp, MJ/kg ^b		400°C	1.28
density, g/cm ³		550°C	1.26
solid		electrical resistivity,	
at 20°C	0.968	μΩ·cm	
50°C	0.962	solid	
mp	0.951 ^c	at 20°C	4.69
liquid		mp	6.60 ^c
at mp	0.927	liquid	
400°C	0.856	at mp	9.64
550°C	0.820	400°C	22.14
viscosity, mPa·s (=cP)		550°C	29.91
at 100°C	0.680	thermal conductivity,	
400°C	0.284	W/(m·K)	
550°C	0.225	solid	
surface tension,		at 20°C	1323
mN/m (=dyn/cm)		mp	1193 ^c
at mp	192	liquid	
400°C	161	at mp	870
550°C	146	400°C	722
		550°C	648

^aRef. 5.^bTo convert J to cal, divide by 4.184.^cValue is estimated.

a suitable base for high surface sodium. Other powders, eg, sodium chloride, hydride, monoxide, or carbonate, can also be used.

The solid to be coated is placed in a vessel equipped with a stirrer, filled with pure, dry nitrogen or another inert gas, and heated to 110–250°C. Clean sodium is added with stirring. If enough is added, the sodium is rapidly distributed over the entire available surface. Depending on that available surface, up to 30 wt % or more sodium can be added without changing the free-flowing character of the system (7,8).

Chemical Properties

Sodium forms unstable solutions in liquid ammonia, where a slow reaction takes place to form sodamide and hydrogen, as follows:



Iron, cobalt, and nickel catalyze this reaction. The rate depends on temperature and sodium concentration. At -33.5°C, 0.251 kg sodium is soluble in 1 kg ammonia. Concentrated solutions of sodium in ammonia separate into two liquid

phases when cooled below the consolute temperature of -41.6°C . The compositions of the phases depend on the temperature. At the peak of the conjugate solutions curve, the composition is 4.15 atom % sodium. The density decreases with increasing concentration of sodium. Thus, in the two-phase region the dilute bottom phase, low in sodium concentration, has a deep-blue color; the light top phase, high in sodium concentration, has a metallic bronze appearance (9-13).

At high temperature, sodium and its fused halides are mutually soluble (14). The consolute temperatures and corresponding Na mol fractions are given in Table 3. Nitrogen is soluble in liquid sodium to a very limited extent, but sodium has been reported as a nitrogen-transfer medium in fast-breeder reactors (5) (see NUCLEAR REACTORS).

Table 3. Mutual Solubility of Sodium and Fused Sodium Halides

Compound	Consolute temperature, $^{\circ}\text{C}$	Na concentration, mol fraction
Na-NaF	1182	0.28
Na-NaCl	1080	0.50
Na-NaBr	1025	0.52
Na-NaI	1033	0.50

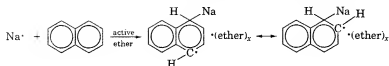
The solubility-temperature relationships of sodium, sodium compounds, iron, chromium, nickel, helium, hydrogen, and some of the rare gases are important in the design of sodium heat exchangers, especially those used in liquid-metal fast-breeder reactors (LMFBR). The solubility of oxygen in sodium is particularly important because of its marked effect on the corrosion of containment metals and because of problems of plugging narrow passages. This solubility S given in units of ppmwt O is

$$\log S = 6.239 - 2447/T \quad (2)$$

for temperature, T , in Kelvin from about 400 to 825 K (5). Solubility data for many other materials in sodium are also available (5). Because metallic calcium is always present in commercial sodium, and to a lesser extent in nuclear-grade sodium, the solubilities of calcium oxide and nitride in sodium are critical to the design of heat-transfer systems. These compounds are substantially insoluble at $100-120^{\circ}\text{C}$ (15) (see HEAT-EXCHANGE TECHNOLOGY).

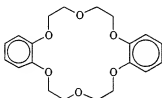
Sodium is soluble in ethylenediamine (16,17), but solubility in other amines such as methyl- or ethylamine may require the presence of ammonia. Sodium solubility in ammonia and ethylenediamine solutions has been extensively investigated (18). Sodium is insoluble in most hydrocarbons and is readily dispersed in kerosene or similar liquids toward which it is chemically inert. Such dispersions provide a reactive form of the metal.

In 1932 a class of complexes consisting of ethers, sodium, and polycyclic hydrocarbons was discovered (19). Sodium reacts with naphthalene in dimethyl ether as solvent to form a soluble, dark-green, reactive complex. The solution is electrically conductive. The reaction has been described as follows (8):



The addition product, $\text{C}_{10}\text{H}_8\text{Na}$, called naphthalenesodium or sodium naphthalene complex, may be regarded as a resonance hybrid. The ether is more than just a solvent that promotes the reaction. Stability of the complex depends on the presence of the ether, and sodium can be liberated by evaporating the ether or by dilution using an indifferent solvent, such as ethyl ether. A number of ether-type solvents are effective in complex preparation, such as methyl ethyl ether, ethylene glycol dimethyl ether, dioxane, and THF. Trimethylamine also promotes complex formation. This reaction proceeds with all alkali metals. Other aromatic compounds, eg, diphenyl, anthracene, and phenanthrene, also form sodium complexes (16,20).

In 1967, DuPont chemist Charles J. Pedersen (21) discovered a class of ligands capable of complexing alkali metal cations, a discovery which led to the Nobel Prize in Chemistry in 1987. These compounds, known as crown ethers or cryptands, allow greatly enhanced solubility of sodium and other alkali metals in amines and ethers. About 50 crown ethers having between 9–60 membered oligoether rings were described (22). Two such structures, dibenzo-18-crown-6 (1) and benzo-9-crown-3 (2), are shown.



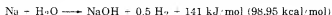
(1)



(2)

Sodium Reactions. Sodium reacts with many elements and substances (5,16,20) and forms well-defined compounds with a number of metals. Some of these alloys are liquid below 300°C . When heated in air, sodium ignites at about 120°C and burns with a yellow flame, evolving a dense white acrid smoke. In the presence of air or oxygen a monoxide or peroxide is formed. Limited oxygen supply and temperatures below 160°C give sodium monoxide, Na_2O , as the principal reaction product. At 250 – 300°C in the presence of adequate oxygen, sodium peroxide, Na_2O_2 , is formed along with very small amounts of superoxide, NaO_2 (see PEROXIDES AND PEROXIDE COMPOUNDS, INORGANIC PEROXIDES). Sodium superoxide is made from sodium peroxide and oxygen at high temperature and pressure. Sodium does not react with extremely dry oxygen or air, except for the possible formation of a surface film of transparent oxide (23).

The reaction of sodium and water according to the following equation



has been extensively studied as it relates to the generation of steam in sodium-cooled breeder reactors (5). Under ordinary circumstances, this reaction is very rapid. The liberated heat melts the sodium and frequently ignites the evolved hydrogen if air is present. In the absence of air and a large excess of either reactant, the reaction may be relatively nonviolent. Thus, dry steam or superheated steam may be used to clean equipment contaminated with sodium residues, but precautionary action must be taken to exclude air, avoid condensation, and design equipment to drain without leaving pockets of sodium. Any such sodium may become isolated by a layer of solid sodium hydroxide and can remain very reactive and hazardous.

Hydrogen and sodium do not react at room temperature, but at 200–350°C sodium hydride is formed (24,25). The reaction with bulk sodium is slow because of the limited surface available for reaction, but dispersions in hydrocarbons and high surface sodium react more rapidly (7). For the latter, reaction is further accelerated by surface-active agents such as sodium anthracene-9-carboxylate and sodium phenanthrene-9-carboxylate (26–28).

There is very little evidence of the direct formation of sodium carbide from the elements (29,30), but sodium and graphite form lamellar intercalation compounds (16,31–33). At 500–700°C, sodium and sodium carbonate produce the carbide, Na_2C_2 ; above 700°C, free carbon is also formed (34). Sodium reacts with carbon monoxide to give sodium carbide (34), and with acetylene to give sodium acetylide, NaHC_2 , and sodium carbide (disodium acetylide), Na_2C_2 (see CARBIDES) (8).

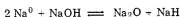
Nitrogen and sodium do not react at any temperature under ordinary circumstances, but are reported to form the nitride or azide under the influence of an electric discharge (14,35). Sodium silicide, NaSi , has been synthesized from the elements (36,37). When heated together, sodium and phosphorus form sodium phosphide, but in the presence of air with ignition sodium phosphate is formed. Sulfur, selenium, and tellurium form the sulfide, selenide, and telluride, respectively. In vapor phase, sodium forms halides with all halogens (14). At room temperature, chlorine and bromine react rapidly with thin films of sodium (38), whereas fluorine and sodium ignite. Molten sodium ignites in chlorine and burns to sodium chloride (see SODIUM COMPOUNDS, SODIUM HALIDES).

At room temperature, little reaction occurs between carbon dioxide and sodium, but burning sodium reacts vigorously. Under controlled conditions, sodium formate or oxalate may be obtained (8,16). On impact, sodium is reported to react explosively with solid carbon dioxide. In addition to the carbide-forming reaction, carbon monoxide reacts with sodium at 250–340°C to yield sodium carbonyl, $(\text{NaCO})_6$ (39,40). Above 1100°C, the temperature of the Deville process, carbon monoxide and sodium do not react. Sodium reacts with nitrous oxide to form sodium oxide and burns in nitric oxide to form a mixture of nitrite and hyponitrite. At low temperature, liquid nitrogen pentoxide reacts with sodium to produce nitrogen dioxide and sodium nitrate.

Phosphorus trichloride and pentachloride form sodium chloride and sodium phosphide, respectively, in the presence of sodium. Phosphorus oxychloride, POCl_3 , when heated with sodium, explodes. Carbon disulfide reacts violently, forming sodium sulfide. Sodium amide (sodamide), NaNH_2 , is formed by the reaction of ammonia gas with liquid sodium. Solid sodium reacts only superficially

with liquid sulfur dioxide but molten sodium and gaseous sulfur dioxide react violently. Under carefully controlled conditions, sodium and sulfur dioxide yield sodium hydrosulfite, $\text{Na}_2\text{S}_2\text{O}_4$ (41). Dry hydrogen sulfide gas reacts slowly with solid sodium, but in the presence of moisture the reaction is very rapid. The product is sodium sulfide.

Sodium reacts with dilute acids about as vigorously as it reacts with water. The reaction with concentrated sulfuric acid may be somewhat less vigorous. At 300–385°C, sodium and sodium hydroxide react according to the following equilibrium:



The reaction is displaced to the right by dissociation of sodium hydride and liberation of hydrogen. This dissociation is favored under vacuum or when the reaction zone is swept with an inert gas to remove the hydrogen (24,25). In this manner, sodium monoxide substantially free of sodium and sodium hydroxide is produced. In the more complicated reaction between sodium metal and anhydrous potassium hydroxide, potassium metal and sodium hydroxide are produced in a reversible reaction (42,43):



Superimposed on this simple equilibrium are complex reactions involving the oxides and hydrides of the respective metals. At about 400°C, the metal phase resulting from the reaction of sodium and potassium hydroxide contains an unidentified reaction product that precipitates at about 300°C (15).

Data for the free energy of formation (44,45) indicate that sodium reduces the oxides of Group 1 (IA) elements except lithium oxide. Sodium does not reduce oxides of Group 2 (IIA) elements, but does reduce the Group 12 (IIB) mercury, cadmium, and zinc oxides. Many other oxides are reduced by metallic sodium. In some cases reduction depends on the formation of exothermic complex oxides. Iron oxide is reduced by sodium below ca 1200°C. Above this temperature the reaction is reversed. Sodium reduces most fluorides except the fluorides of lithium, the alkaline earths, and some lanthanides. It reduces most metallic chlorides, although some of the Group 1 (IA) and Group 2 (IIA) chlorides give two-phase equilibrium systems consisting of fused salt and alloy layers (43). Some heavy metal sulfides and cyanides are also reduced by sodium.

Sodium reacts with many organic compounds, particularly those containing oxygen, nitrogen, sulfur, halogens, carboxyl, or hydroxyl groups. The reactions are violent in many cases, for example, organic halides. Carbon may be deposited or hydrogen liberated, and compounds containing sulfur or halogens usually form sodium sulfide or sodium halides. Alcohols give alkoxides (see ALKOXIDES, METAL). Primary alcohols react more rapidly than secondary or tertiary. The reactivity decreases with increasing number of alcohol carbon atoms, or higher concentrations.

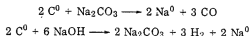
Organosodium compounds are prepared from sodium and other organometallic compounds or active methylene compounds by reaction with

organic halides, cleavage of ethers, or addition to unsaturated compounds. Some aromatic vinyl compounds and allylic compounds also give sodium derivatives.

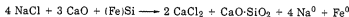
Sodium does not react with anhydrous ethyl ether but may react with higher ethers or mixed ethers. Organic acids give the corresponding salts with evolution of hydrogen or decompose. Pure, dry, saturated hydrocarbons, eg, xylene, toluene, and mineral oil, do not react with sodium at the hydrocarbon-cracking temperature. In the presence of unsaturated hydrocarbons, sodium may add at a double bond or cause polymerization. Sodium amalgam or sodium and alcohol are employed for organic reductions. Sodium is also used as a condensing agent in acetoacetic ester and malonic ester syntheses and the Wurtz-Fittig reaction (16,21) (see MALONIC ACID AND DERIVATIVES).

Manufacture

Thermal Reduction. Metallic sodium is produced by thermal reduction of several of its compounds. The earliest commercial processes were based on the carbon reduction of sodium carbonate (46-49) or sodium hydroxide (1,8,50):



Sodium chloride is reduced by ferrosilicon in the presence of lime:



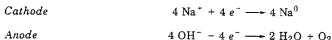
This process was operated briefly in vacuum retorts by Union Carbide in 1945 (51).

The chloride is also reduced by calcium carbide at 800-1200°C under vacuum (52).



A number of other thermal reductions are described in the literature (8), but it is doubtful that any have been carried out on commercial scale.

Electrolysis of Fused Sodium Hydroxide. The first successful electrolytic production of sodium was achieved with the Castner cell (2):



The water formed at the anode diffuses to the cathode compartment where it reacts with its equivalent of sodium:

